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# Magnetorheology of Polymer Systems

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Additional information is available at the end of the chapter

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## Abstract

The results of researches of a magnetic field effect on rheological properties of both paramagnetic, and diamagnetic polymer systems are described. Influence of intensity and the direction of power lines of the magnetic field on the viscosity of magnetic liquids and magnetorheological suspensions is analyzed. Results of theoretical researches of the magnetic field effect on the diamagnetic macromolecule orientation in solutions are discussed. The data on the influence of the magnetic field on rheological parameters of cellulose ether solutions are generalized and analyzed. The rheological parameters are compared with a change of studied system structure under magnetic field. The concentration dependences of viscosity and the sizes of supramolecular particles in solutions are compared. The rheological behavior of systems in a region of phase transitions is considered. Concentration dependences of the viscosity are described by curves with a maximum which concentration corresponds to a phase transition concentration.

**Keywords:** polymer systems, magnetic field, rheology, structure

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## 1. Introduction

There are two classes of substances with various magnetic properties; paramagnetics and diamagnetics. Paramagnetic placed in a magnetic field with an intensity of  $H$  is magnetized in the direction coinciding with the direction of power lines of the field. Thus, a magnetic moment  $\mu$  arises in a sample. The paramagnetism is caused by the orientation of the magnetic moments of atoms and molecules of the paramagnetic under the field. At the same time  $\mu = \chi_{\text{par}}H$ , where  $\chi_{\text{par}}$  is a paramagnetic susceptibility,  $\chi_{\text{par}} \gg 0$ . The paramagnetic particles distributed in the liquids are oriented along the force lines of the external field that leads to an aggregation of particles and to a viscosity growth of such systems (magnetic liquids).

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An increase in the viscosity of magnetic liquids under application of a magnetic field (the magnetorheological effect [1]) was discovered experimentally in the 1950s [2] for the systems based on iron carbonyl and iron oxide. Subsequently, this phenomenon was studied in some reports [3–15]. It was found that, in resting compositions, a structure formation is observed as a result of the magnetodipole interaction of particles and orientation of anisodiametrical structural elements along magnetic force lines. As the shear rate increases, the aggregates break up. Each combination of the given parameters (the viscosity of dispersion medium, the magnetic properties of particles, the field strength, and the shear rate) is characterized by a certain set of structural elements and their mutual disposition. An important feature of the rheological properties of ferrofluids in the magnetic field is their dependence on the mutual orientation of shear and magnetic field. An increment of the effective viscosity of a medium at the perpendicular orientation substantially exceeds the effective viscosity induced by a parallel field. A strong anisotropy of rheological properties upon field orientation along the flow rate, along its gradient, and along the direction of its vortex was revealed in [15]. The new experimentally observed phenomena for ferrofluids are the Weissenberg effect [16], which was detected earlier only in polymer and liquid crystalline media, and the shear-induced reduction in the degree of anisotropy of the internal structure of ferrofluids, as was revealed by small-angle neutron scattering [17]. The effect of magnetic field and surfactants on the rheological properties of strontium ferrite suspensions was studied in [18]. It was shown that, under application of the field, the viscosity of the suspension increases. This phenomenon was explained by the formation of three-dimensional chain structures from the ferrite particles. After the field is switched off, these structures do not decompose fully, and this circumstance is responsible for the hysteresis of suspension viscosity. After introduction of polyelectrolytes into a suspension, its viscosity decreases both in the field and after its switching off. This is caused by a decrease in the interparticle friction and weakening of the strength of three-dimensional structures owing to the formation of a double electrical layer on the surface of particles. In [19], the magnetoviscous properties of two types of magnetic fluids based on iron oxide  $\text{Fe}_3\text{O}_4$  were compared: the first one included oleic acid as a surfactant, and in the second one, the surfactant was tetramethylammonium hydroxide. It was shown that the type of surfactant strongly affects the fluid behavior in the magnetic field: in the presence of oleic acid, a change in viscosity under application of the magnetic field occurs more rapidly than that in the presence of tetramethylammonium hydroxide. The rheological properties of magnetic fluids ferroparticles-poly( $\alpha$ -olefins)-polyurethane, ferroparticles-*n*-octyl-pyrrolidone-butyl acrylate, and ferroparticles-*n*-octylpyrrolidone-pentafluorostyrene were studied in [20]. Recent advances in the field of magnetic fluids were highlighted in reviews [1, 21–26].

To understand the internal physical nature of the magnetoviscous effect, new data on the effect of magnetic field and deforming flow on the dynamics of these systems are required. For example, up to now, the data on the effect of concentration of a magnetic fluid and the rate of its deformation on the magnetorheological effect have been scarce. Papers [24, 25, 27, 28] deal with the concentration dependence of the effect of a constant magnetic field on the viscosity of aqueous and water-glycerol magnetic fluids based on iron and iron oxide nanoparticles. It was shown that the magnetic field enhances the fluid viscosity by 20–80 times. The concentration dependence of the relative viscosity  $\eta/\eta_0$  ( $\eta$  and  $\eta_0$  are the viscosities in the field and in its

absence, respectively) is described by a curve with a maximum. This is explained by the transition from chain aggregates of nanoparticles to drop-shaped ones. The magnetic field with force lines oriented perpendicularly to the rotor rotation axis increases the viscosity of systems to a much higher extent than upon parallel orientation. However the data on magnetorheological properties of the paramagnetic systems containing polymers are not numerous [20, 29].

Diamagnetism is an appearance in substance of a magnetic moment directed toward to the external field, at the same time  $\chi_{\text{diam}} \ll 0$ . Molecules (atoms) of diamagnetic substances have not any unpaired electrons. The theoretical and experimental investigations of interaction of diamagnetic macromolecules with a magnetic field are currently under development [30–64]. It was found experimentally that application of a magnetic field leads to an orientation of macromolecules and their associates along the force lines, to the increase in phase transition temperatures, causes a formation of domains in solutions.

If an anisotropic macromolecule is placed in a magnetic field, then a force acts on it and causes its rotation. The magnetic anisotropy of chemical bonds is responsible for the magnetic anisotropy of the molecule. In polymer systems, the amount of contacts between macromolecules is high; therefore, an orientation of polymer chains proceeds cooperatively. The effect of the field consists in the rotation (orientation) of macromolecular domains in a certain predominant direction that depends on the sign of diamagnetic susceptibility anisotropy  $\Delta\chi^M$  for this polymer. Domains are taken to mean the anisotropic associates of macromolecules or mesophase regions. The diamagnetic moment appearing at the domain under magnetic field can be written as [32, 34]:

$$\mu = \frac{\Delta\chi^M}{2\mu_0} B^2 V \sin 2\xi \quad (1)$$

where  $V$  is domain volume,  $\mu_0$  is a magnetic constant of vacuum,  $B$  is a vector of magnetic induction,  $\xi$  is an angle between the direction  $B$  and the domain axis.

Interaction of external magnetic field with the domain having the magnetic moment  $\mu$  increases energy of magnetic field by value of  $E_{\text{mag}}$  [31]:

$$E_{\text{mag}} = -\left(\frac{1}{2}\right)V\chi_{\perp}^M\mu_0^{-1}B^2 - \left(\frac{1}{2}\right)V\Delta\chi^M\mu_0^{-1}B^2\cos^2\xi \quad (2)$$

where  $\chi_{\perp}^M$  diamagnetic susceptibility in the direction perpendicular to domain axis.

Magnetic orientation is observed when  $E_{\text{mag}}$  exceeds the value of thermal energy ( $k_B T$ ),  $k_B$  is the Boltzmann's constant,  $T$  represents the absolute temperature. From here it follows [31]:

$$V > \frac{2k_B T\mu_0}{|\Delta\chi^M|B^2} \quad (3)$$

This equation determines the minimal critical volume capable to orientation.

The rotational moment of the domain ( $N$ ) is expressed as [35]:

$$N = V\Delta\chi^M \mu_0^{-1} B^2 \sin \xi \cos \xi \omega \quad (4)$$

$\omega$  is normal vector to  $\mathbf{B}$  and domain axis.

Therefore, it is necessary for the orientation of a diamagnetic particle to satisfy the following conditions: a particle must be anisodiametric; the particle volume must be higher than the corresponding critical value  $V_{cr}$ ; and the medium must be low-viscosity. The particles can also be microfibers, crystallites, liquid crystals and other heterogeneous particles suspended in a liquid medium.

In the 1960s, the effect of a magnetic field on liquid crystals was theoretically studied by de Gennes and Meuer [65, 66]. It was shown that, at the critical magnetic field strength, the complete transition of a cholesteric liquid crystal to a nematic one is realized. Experimentally, this was confirmed for liquid crystals of rigid-chain polymer poly( $\gamma$ -benzyl-L-glutamate) in a number of solvents in the 1970s [67, 68]. This phenomenon was explained by the orientation of liquid crystal molecules relative to force lines of the magnetic field.

Since 2006, researchers of the Chair of Macromolecular Compounds, Ural State University (since 2011 Ural Federal University), have been involved in systematic investigations of the effect of magnetic field on the phase transitions, structure, and rheological properties of liquid crystalline solutions of cellulose ethers. It was found [57–64] that application of a magnetic field leads to a change in the type of liquid crystals from cholesteric to nematic, causes formation of domains in solutions, and entails a substantial (by tens of degrees) increase in the temperature of formation of liquid crystalline phases. As the molecular mass of a polymer is increased, the ability of its molecules to orientate in the magnetic field is reduced. The solutions of cellulose ethers represent memory systems: after termination of magnetic field exposure, the orientation of macromolecules and the increased phase-transition temperature are preserved for many hours. The magnetic field leads to an increase in the sizes of associates of rigid-chain macromolecules and in the viscosity of solutions.

It should be noted that up to now there is only one theoretical [69] and some experimental works [70–76] in which an influence of the magnetic field on rheological properties of polymer solutions is considered. Note that practically no information is available on the relaxation character of the rheological behavior of polymer solutions in the magnetic field.

Therefore, the main aim of this study is to investigate the magnetorheological properties of paramagnetic and diamagnetic polymer systems

## 2. Results and discussion

### 2.1. Materials and methods

The magnetically sensitive systems (suspensions of aerosil and iron nanoparticles) in poly(ethylene glycol) (PEG) and poly(dimethylsiloxane) (PDMS) have been studied. The nanodispersed iron powder ( $d_w = 150$  nm), nanodispersed aerosil ( $d_w = 250$  nm), PEG with



$M_n = 400$  and PDMS with  $M_n = 3.4 \times 10^4$  were used. The suspensions were prepared by mixing of PEG and PDMS with aerosil nanoparticles (systems 1 and 2, respectively). The concentrations of aerosil were 4.2 and 2.0 wt% in systems 1 and 2, respectively. The magnetic fluids have been produced by addition of iron nanoparticles to basic suspensions.

Hydroxypropyl cellulose samples with  $M_w = 1 \times 10^5$  and a degree of substitution of  $\alpha = 3.2$  (HPC1), with  $M_w = 1.6 \times 10^5$  and  $\alpha = 3.6$  (HPC2), ethyl cellulose (EC) sample with  $M_n = 2.6 \times 10^4$  and  $\alpha = 2.6$  have been investigated. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol and ethylene glycol were used as solvents. The purities of the solvents were confirmed by their refractive indexes. Polymer solutions were prepared in sealed ampoules for several weeks at 368 K (in DMSO), 333 K (in ethanol), 353 K (in DMF) and 363 K (in ethylene glycol).

The phase state of solutions was estimated with the use of an OLYMPUS BX-51 polarization microscope. The radii of supramolecular particles,  $r$ , in moderately concentrated and concentrated solutions were determined via the method of the turbidity spectrum, which was suggested by Heller et al. [77–79] and developed by Klenin et al. [80]. Optical density  $A$  of solutions was measured with Helios spectrophotometers. The said method is based on the Angstrom eq  $A \sim \lambda^{-n}$ , where  $\lambda$  is the wavelength of light passing through a solution and  $n$  is a composite function that depends on the relative refractive index of a solution,  $m_{rel}$ , and coefficient  $\alpha$  related to dimensions of light-scattering particles:

$$n = \frac{d \ln A}{d \ln \lambda} \quad (5)$$

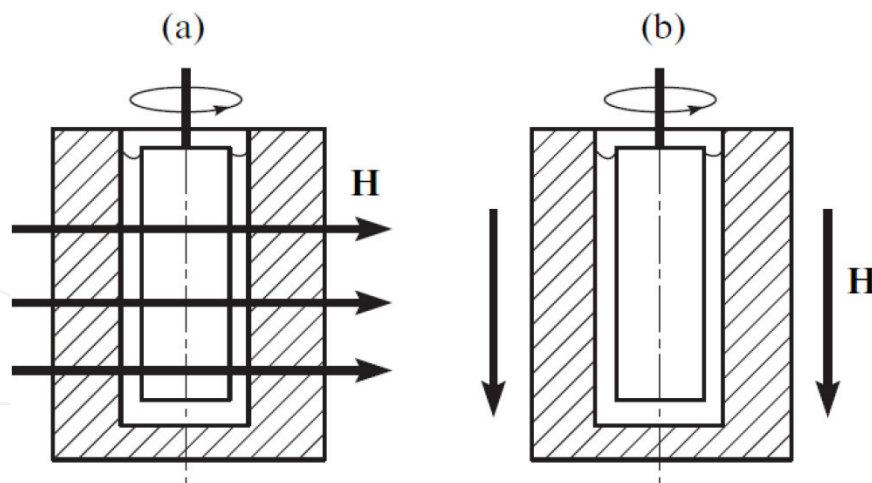
For every solution, relationships  $\ln A$  versus  $\ln \lambda$  were plotted, and the value of  $n$  was calculated from the slope of the straight line. The relative refractive index was calculated through the equation  $m_{rel} = n_{D \text{ pol}} / n_{D \text{ sol}}$ , where  $n_{D \text{ pol}}$  and  $n_{D \text{ sol}}$  are the refractive indexes of a polymer and solvent, respectively. With the use of the tabulated data from [80], parameter  $\alpha$  was determined for the found values of  $m_{rel}$  and  $n$ . Parameter  $\alpha$  is related to average weighed radius  $r_w$  of scattering particles via the expression:

$$\alpha = \frac{2\pi r_w}{\lambda_{av}} \quad (6)$$

In this expression, the wavelength of light passing through a solution is  $\lambda_{av} = \lambda_{av} / n_{D \text{ sol}}$ , where  $\lambda_{av}$  is the wavelength of light in vacuum corresponding to the midpoint of the linear portion of the  $\ln A - \ln \lambda$  plot.

Solution viscosities under a magnetic field and in its absence were measured on a Rheotest RN 4.1 rheometer modified by us (**Figure 1**).

Rheometer was equipped with a coaxial-cylindrical operating unit made of a poorly magnetic substance, brass. Two magnets were used: the first producing a magnetic field with an intensity of 3.7 kOe and lines of force perpendicular to the rotor-rotation axis and the second one producing a magnetic field with an intensity of 3.6 kOe and lines of force parallel to the rotor-rotation axis. A metallic rotor rotating in a magnetic field can be considered as a current generator closed upon itself [81]. The working generator produces



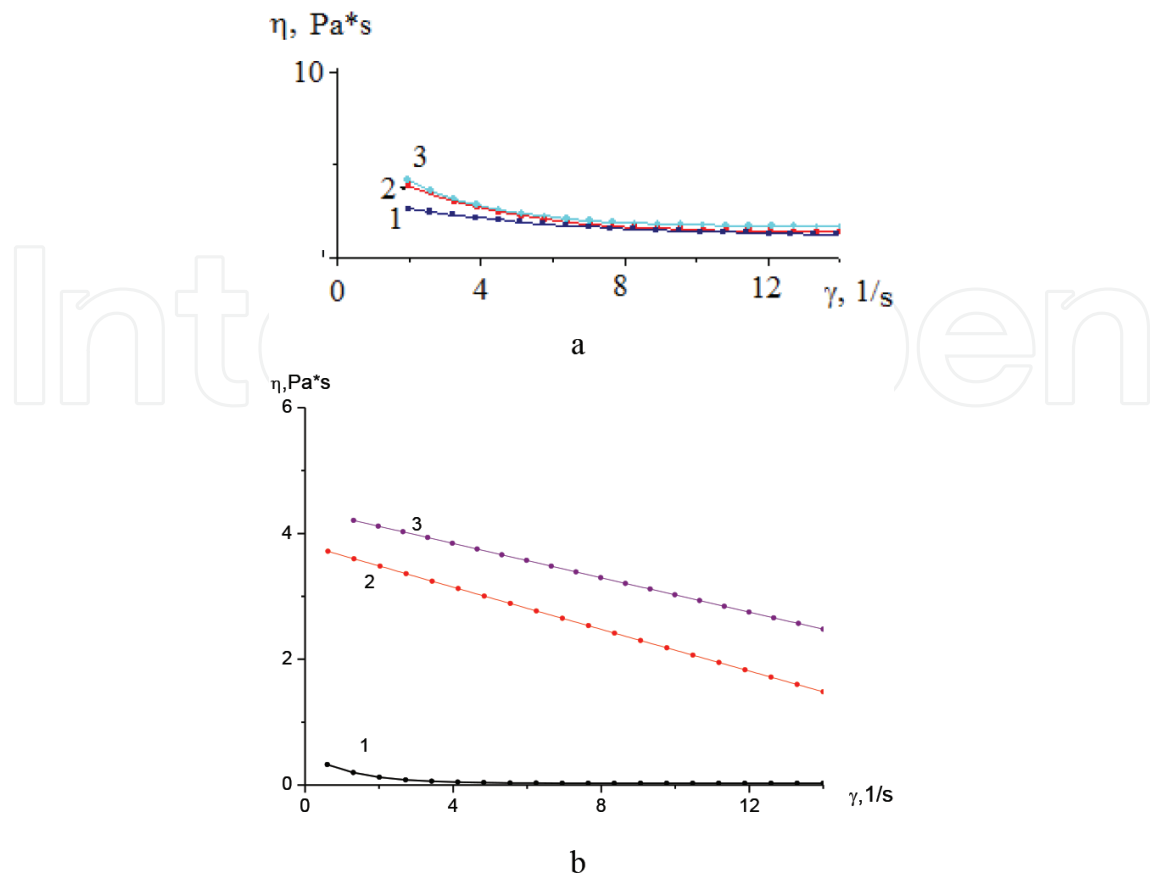
**Figure 1.** Schematic representation of viscosity determination with field lines directed (a) perpendicularly and (b) parallel to the rotor-rotation axis.

a braking torque. To take into account this torque, a correction dependence of shear stress on shear rate in the working unit filled with air between the cylinder surfaces was plotted. The true shear stress for solutions was obtained as the difference between the measured value and the correction value at the same shear rate. The relaxation character of rheological behavior of polymer solutions was studied via two-stage measurements: during an increase in shear rate from 0 to  $13 \text{ s}^{-1}$  (loading) for 10 min followed by a decrease in shear rate from 13 to  $0 \text{ s}^{-1}$  (unloading) for 10 min.

## 2.2. Magnetorheological properties of paramagnetic systems containing polymers

The dependences of viscosities of PEG-aerosil and PDMS-aerosil suspensions on the shear rate in the magnetic field and in its absence are depicted in **Figure 2**.

As the shear rate increases, the viscosity of the suspensions decreases. This fact provides evidence for the destruction of the initial structure of systems. The magnetic field has almost no effect on the viscosity of the suspensions of oligomeric PEG-aerosil upon either parallel or perpendicular orientation of magnetic force lines relative to the rotor rotation axis. An analogous phenomenon was observed for the glycerol-aerosil system [24]. However, the viscosity of the PDMS-aerosil system in the field grows substantially, although the viscosity of PDMS does not change in a magnetic field. An increase in the viscosity of polymer solutions under application of a magnetic field is observed for a series of cellulose ether-solvent systems, i.e., for the polymers with the moderate chain rigidity [70–76]. According to the developed theory of interaction between diamagnetic macromolecules and their associates with the magnetic field [31–33], the effect of the field can manifest itself under the following conditions: a particle must be anisodiametrical; the particle volume must be higher than the corresponding critical value  $V_{cr}$ ; and the medium must be low-viscosity. The aggregates of aerosil particles bound by PDMS macromolecules may correspond to the first two conditions, so the viscosity of the PDMS-aerosil system in the field grows substantially, in conformity with the latter condition.



**Figure 2.** Dependences of the viscosity on the shear rate for the (a) PEG-aerosil and (b) PDMS-aerosil suspensions.  $H = 0$  (1),  $H_{\perp} = 3.7$  (2), and (3)  $H_{\parallel} = 3.6$  kOe (3).

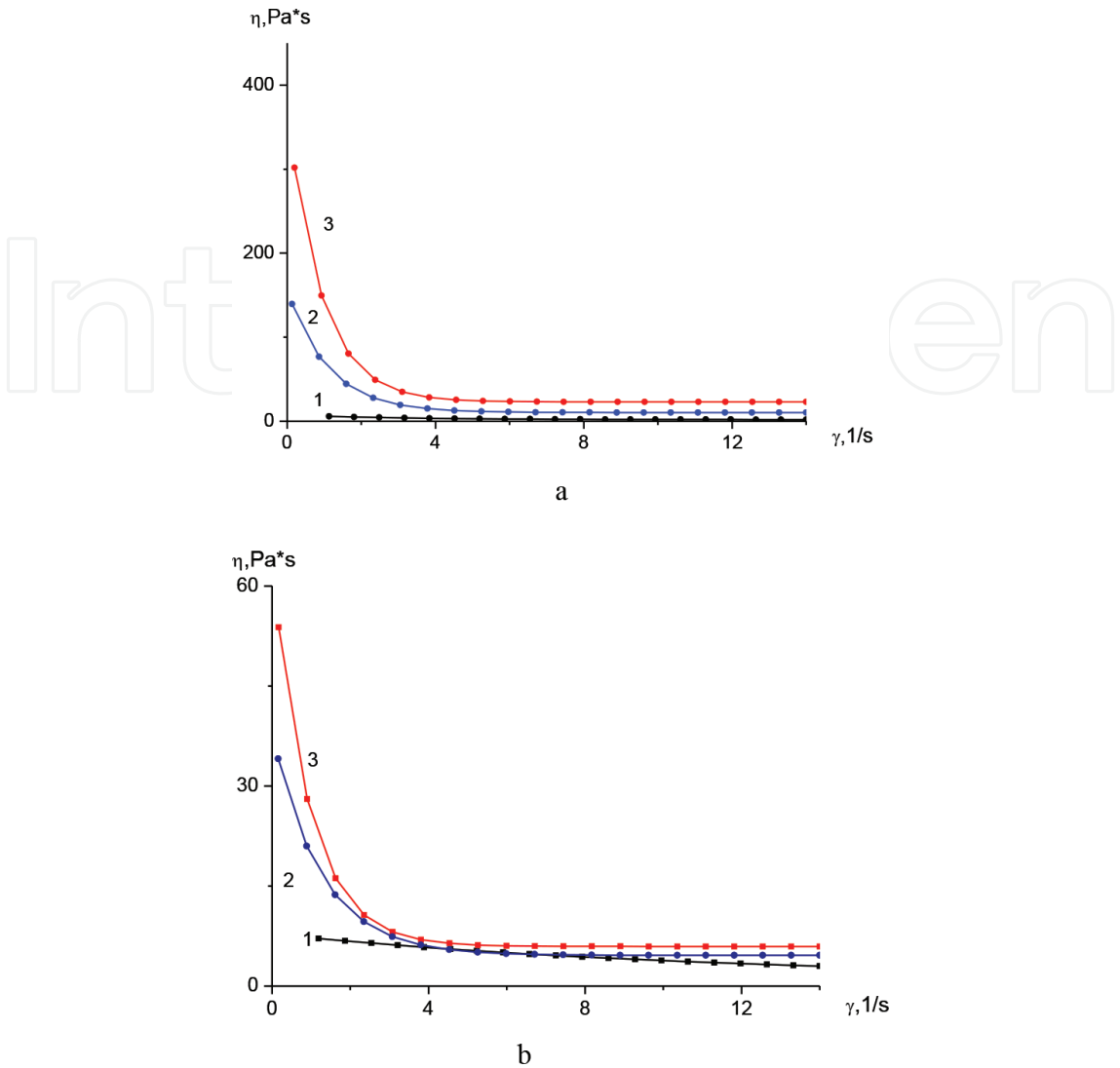
**Figure 3** shows the dependences of the viscosity on  $\dot{\gamma}$  for suspensions with the concentrations of iron nanoparticles of 7.4 wt % (system 1) and 5.7 wt % (system 2) in the magnetic field and in its absence.

An analogous dependence was obtained for all other explored suspensions with ferroparticles. Under application of the magnetic field, the aggregates of iron nanoparticles are formed. This leads to a substantial increase in viscosity at low shear rates ( $\dot{\gamma} < 1 \text{ s}^{-1}$ ). As the shear rate increases from 1 to  $14 \text{ s}^{-1}$ , the aggregate destruction and the nanoparticle orientation occur; as a result, the viscosity decreases. In this respect, further analysis of the field effect on the properties of the system was carried out using the viscosity data obtained at low values of  $\dot{\gamma}$ . The dependences of suspension viscosity on the concentration of iron nanoparticles in the magnetic field are demonstrated in **Figure 4**.

From this figures, it follows that the suspension viscosity substantially increases with the growth of ferroparticle concentration. The viscosity in the transverse field is higher than that in the longitudinal one.

**Figure 5** shows the dependence of relative viscosity  $\eta/\eta_0$  of suspensions on the concentration of ferroparticles ( $\eta$  and  $\eta_0$  are the viscosities in the field and in its absence, respectively).

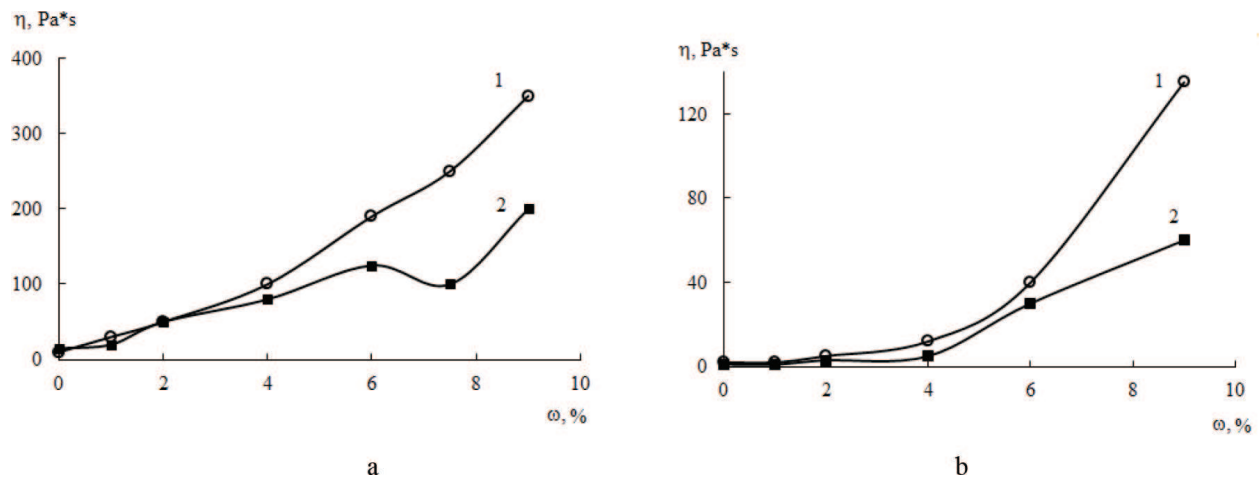




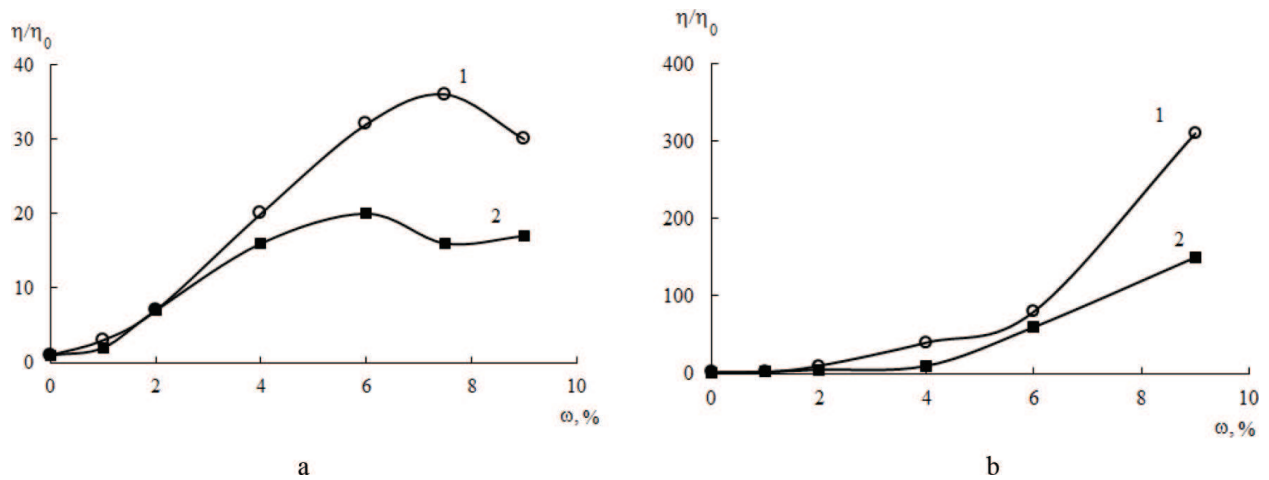
**Figure 3.** Dependences of the viscosity on the shear rate for (a) PEG-Aerosol-Iron nanoparticle and (b) PDMS-Aerosol-Iron nanoparticle suspensions.  $\omega_2 =$  (a) 7.4 and (b) 5.7 wt %. (1)  $H = 0$ , (2)  $H_{II} = 3.6$  and (3)  $H_L = 3.7$  kOe.

The relative viscosity reflects the effect of the magnetic field on the orientation and aggregation of iron nanoparticles. It is obvious that an increase in the concentration of iron nanoparticles, which are able to orient in the field, leads to an increase in viscosity by 18–35 times (system 1) and 120–300 times (system 2). The viscosity of the suspensions in the transverse magnetic field is almost two times higher than that in the longitudinal field. To analyze this phenomenon, let us consider the flow processes of ferrofluids using the schemes presented in **Figure 6**.

If the direction of force lines is perpendicular to the rotor-rotation axis (**Figure 6a**), the orientation of iron nanoparticle aggregates in quadrants I and III coincides with the direction of flow, and the viscosity can decrease. In quadrants II and IV, the orientation of nanoparticles and their aggregates is perpendicular to the direction of flow, and the viscosity must increase. Apparently, in the general case, the viscosity can both decrease and increase. When the direction of force lines



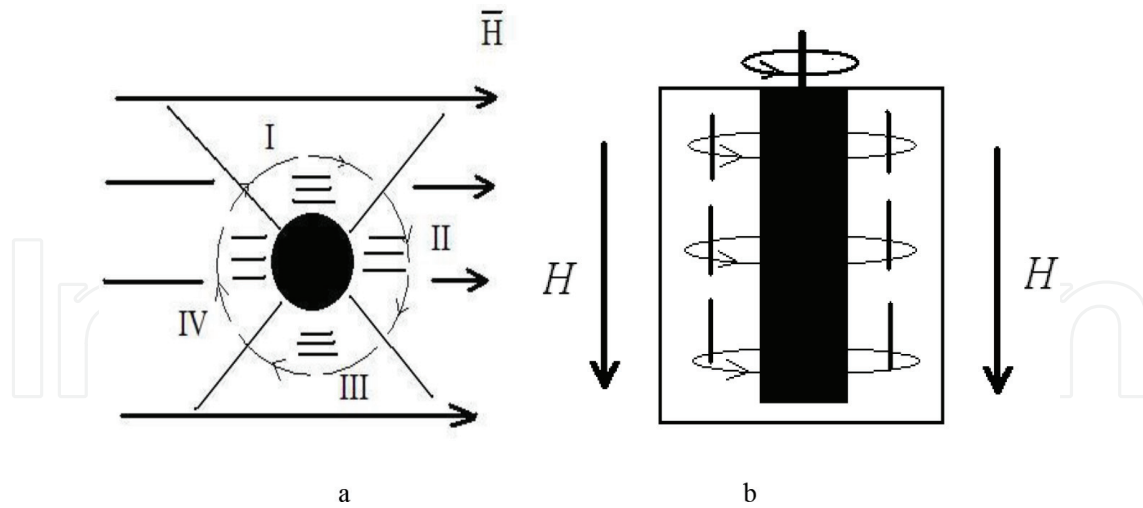
**Figure 4.** Concentration dependences of the viscosity of (a) PEG-Aerosol-Iron nanoparticle and (b) PDMS-Aerosol-Iron nanoparticle suspensions on the concentration of ferroparticles. (1)  $H_{\perp} = 3.7$  and (2)  $H_{\parallel} = 3.6$  kOe.  $\gamma =$  (a) 0.4 and (b) 0.5 s $^{-1}$ .



**Figure 5.** Dependences of the relative viscosity of (a) PEG-Aerosil-Iron nanoparticle and (b) PDMS-Aerosil-Iron nanoparticle suspensions on the ferroparticle concentration. (1)  $H_{\perp} = 3.7$  and (2)  $H_{\parallel} = 3.6$  kOe;  $\gamma =$  (a) 0.4 and (b) 0.5 s $^{-1}$ .

is parallel to the rotor rotation axis (in the longitudinal field) (**Figure 6b**) the aggregates of iron nanoparticles orient by their long axis along the rotor-rotation axis, i.e. layer-by-layer. In this case, an increase in viscosity caused by the aggregation of particles in the magnetic field can be compensated by reduction in the forces of viscous friction owing to the layer-by-layer arrangement of the particles. On the whole, the experiments show that, in the transverse field, the viscosity of suspensions increases to a higher extent than in the longitudinal field.

An initial increase in the effect of the magnetic field on viscosity (**Figure 5**) is connected with growth in the number of particles capable of orientation and subsequent aggregation in the field. However, upon further increase in the concentration of particles, the growth of suspension viscosity now hampers the orientation processes and the effect of the magnetic field becomes weaker. A maximum arises on curves  $\eta/\eta_0 = f(\gamma)$  (**Figure 5a**).

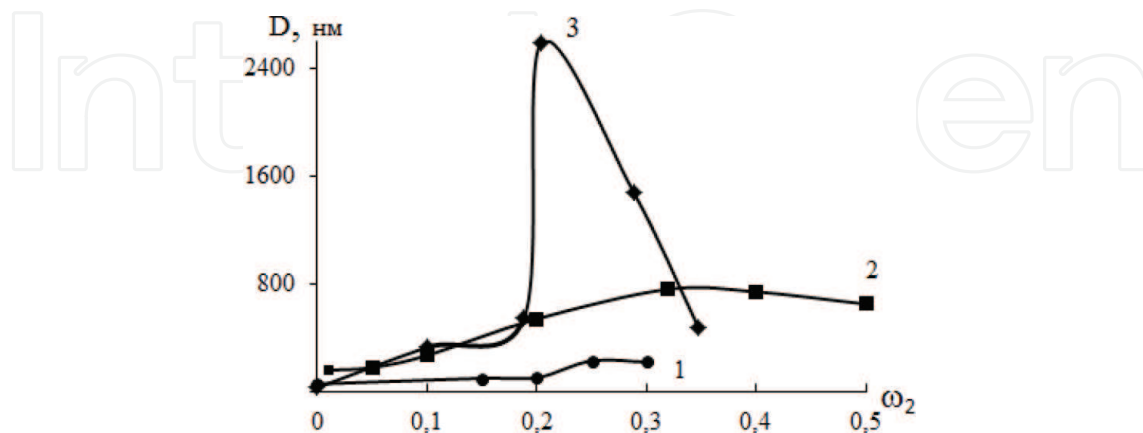


**Figure 6.** Schemes of suspension flow in the magnetic field at (a) perpendicular and (b) parallel directions of force lines relative to the rotor-rotation axis.

### 2.3. Magnetorheological properties and structure of diamagnetic polymer systems

**Figure 7** shows the concentration dependences of the diameters ( $D = 2r$ ) of supramolecular particles in the systems: HPC1-ethylene glycol (1), HPC1-water (2) and EC-DMF (3).

The mean-square distance between chain ends of a macromolecule was calculated via the equations  $h^2 = LA$  ( $L$  is contour length) and  $(h^2)^{1/2} = (LA)^{1/2}$ . In calculations of macromolecule size, the Kuhn segment values  $A = 21.4$  nm for HPC and 16 nm for EC [82], the length of a cellobiose residue of 1.03 nm, and the unit length of a cellulose ether macromolecule of 0.5 nm were used. The contour length of a macromolecule was calculated through eq.  $L = 0.5n$ , where  $n$  is the degree of polymerization. Calculated contour length  $L$  of HPC1 macromolecules and the mean-square distance between chain ends  $(h^2)^{1/2}$  were 164 and 60 nm, respectively, 216 and 68 nm for HPC2 and 56 and 30 nm for EC. From **Figure 7**, it follows that, in solutions with



**Figure 7.** Concentration dependences of the diameters of supramolecular particles in the systems: HPC1-Ethylene glycol (1), HPC1-Water (2) and EC-DMF (3).

concentrations  $\omega_2 > 0.05$ , there are no isolated macromolecules and their associates (supramolecular particle involving a great number of macromolecules) are present, with the sizes of supramolecular particles in EC solutions being 4–10 times larger than those in HPC solutions. This can be caused by a strong interchain interaction and a higher packing density of EC relatively HPC macromolecules. Indeed, the linear ethyl radicals in the polymeric units of neighboring EC macromolecules can produce a denser packing with each other than the branched hydroxypropyl radicals of HPC.

The concentration dependences of  $D$  are described by curves with maxima. The concentrations of solutions with the maximum particle size coincide with the region of the transition from an isotropic solution to an anisotropic solution. In isotropic solutions, macromolecules and their associates are not oriented relative to each other. With an increase in polymer concentration, they form large particles as a result of the intensification of the interchain interaction. The formed large particles do not have a dense packing; i.e., they may contain abundant solvent. During the transition to the LC state with a further increase in the polymer concentration, the emerged orientation of macromolecules and supramolecular particles toward each other leads to increase in interchain interaction. This phenomenon may result in the squeezing out of the solvent from supramolecular particles, an event that is manifested in a decrease in their size. The such phenomenon is revealed for other systems in [83–85].

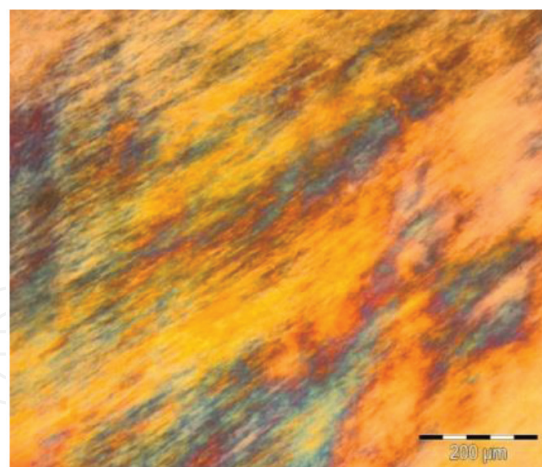
**Figure 8** shows the micrographs of HPC solutions after their treatment with the magnetic field. As is seen, the streaky structure manifests itself, thus indicating formation of large domains in the course of orientation. Similar data were obtained for HPC1 solutions in ethylene glycol.

The our data of researches of a surface relief for the films HPC1 prepared from solutions in ethylene glycol under magnetic field and in its absence are given in **Figure 9** and in a **Table 1**.

**Figure 9** and the **Table 1** show that heterogeneity of the surface relief of HPC1 film is more after processing by magnetic field, than before processing. At the same time on the surface of the film received in the magnetic field an orientation of strips of one height is observed. Therefore the magnetic field causes the orientation processes in solutions, at the same time the domain structure arising in solutions is fixed after evaporation of a solvent and shown in orientation of strips of the film relief.

The application of the magnetic field leads to development of the domain structure as a result of additional orientation of macromolecules in the field. Similar data were obtained for other systems having liquid crystalline transitions [57, 58, 62, 70, 71, 73, 75, 76]. In accordance with [32, 86, 87], macromolecules orient in the magnetic field with their long chains arranged parallel to the force lines. This orientation is related to the molecular diamagnetic anisotropy of macromolecules. As a consequence, supramolecular particles are formed, especially in the vicinity of the LC phase transition [57, 58, 62]. During treatment of solutions with a magnetic field, the particle size grows owing to additional orientation of macromolecules and supramolecular particles relative to the field lines of force and an increase in the interchain interaction.

The concentration dependences of diameters  $D = 2r$  of light scattering particles are depicted in **Figure 10**.



a



b

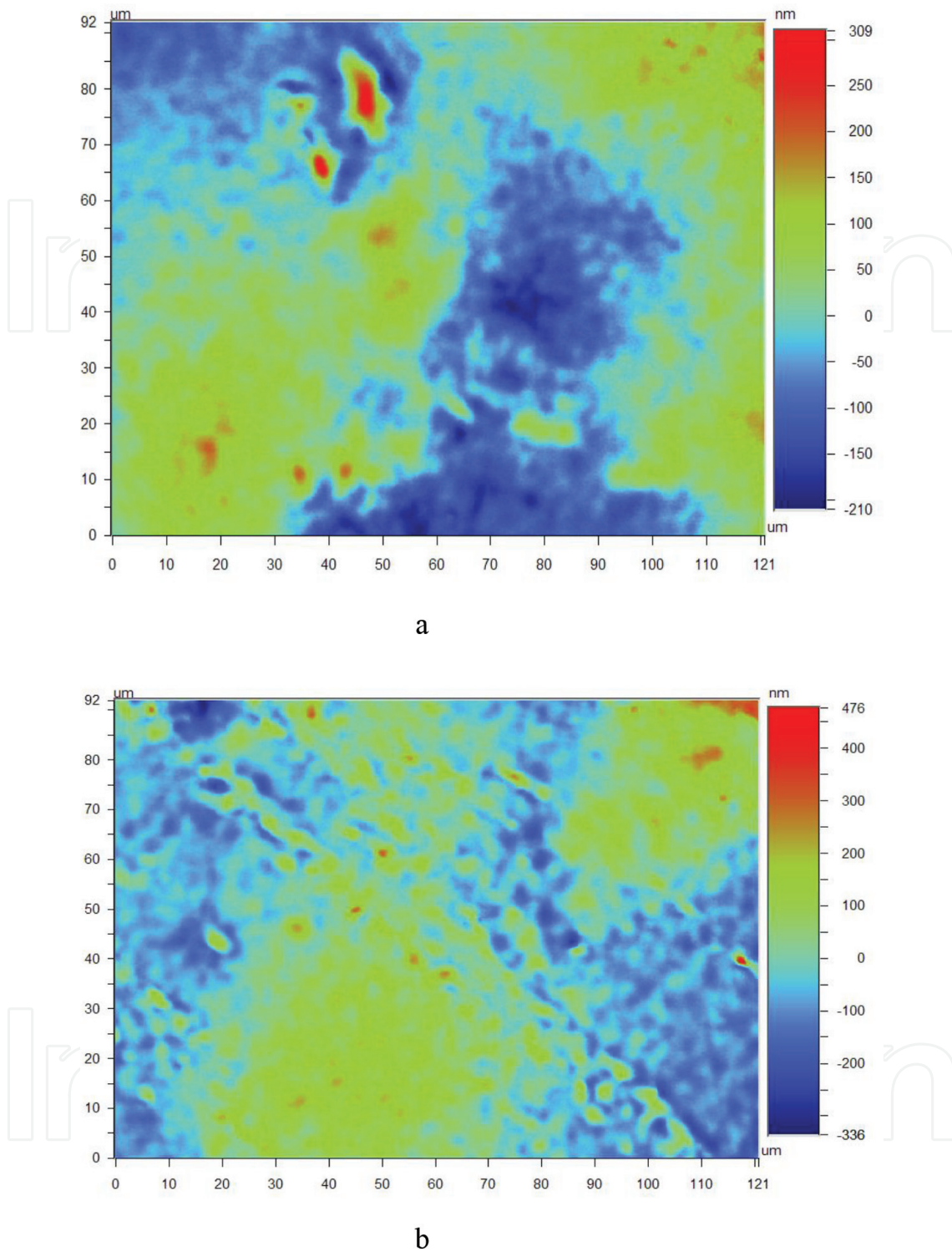
**Figure 8.** Micrographs of solutions under crossed polaroids after their treatment with the magnetic field. a) HPC2-Ethanol,  $\omega_2 = 0.55$ ; b) HPC2-DMSO,  $\omega_2 = 0.50$ .  $H = 3.7 \text{ kOe}$ .

The concentration dependences of  $D$  are described by curves with maxima. The concentrations of solutions with the maximum particle size coincide with the region of the transition from an isotropic solution to an anisotropic solution.

A concentration dependence of relative size  $r/r_0$  of supramolecular particles (where  $r_0$  and  $r$  are the radii of light-scattering particles before and after magnetic-field treatment of solutions, respectively) was found (**Figure 11**).

Note that the solution concentration with the maximum relative size of particles for the EC-DMF system is 2.5 times lower than that for the HPC-ethylene glycol system, an outcome that is due to the larger sizes of supramolecular particles in EC solutions. These dependences reflect the effect of a magnetic field on the orientation of macromolecules and supramolecular particles in solutions. An increasing number of magnetically sensitive macromolecules and supramolecular particles, leads to the intensification of the orientation processes in the field. However, with a further increase in the polymer concentration, the increasing density of the fluctuation network of entanglements begins to hinder the orientation processes and the





**Figure 9.** The micrographs of the surface relief of HPC1 films obtained by a method of an optical interferometry.  $H = 0$  (a),  $H = 3.6 \text{ kOe}$  (b).

influence of the field on the properties of solutions decreases. The similar dependences have been found for the HEC-DMF and EC-DMAA systems earlier [72].

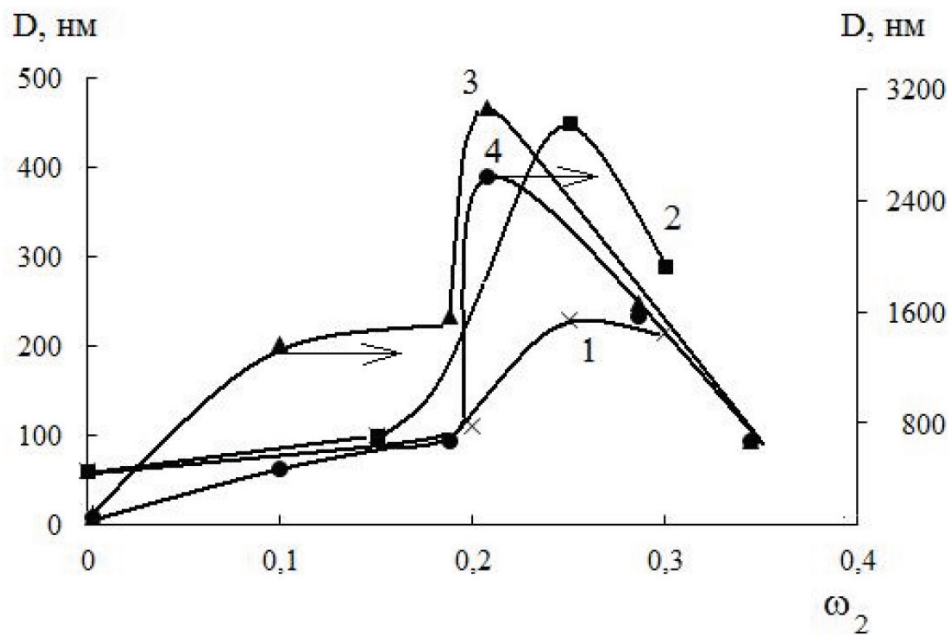
Typical dependences of viscosity of HPC solution on shear rate are presented in **Figures 12** and **13**.



Parameters of the surface relief	Ra	Rq	Rz
Size, nm H=0 kOe	59.47	72.69	480.05
Size, nm H=3.6 kOe	71.99	86.99	629.76

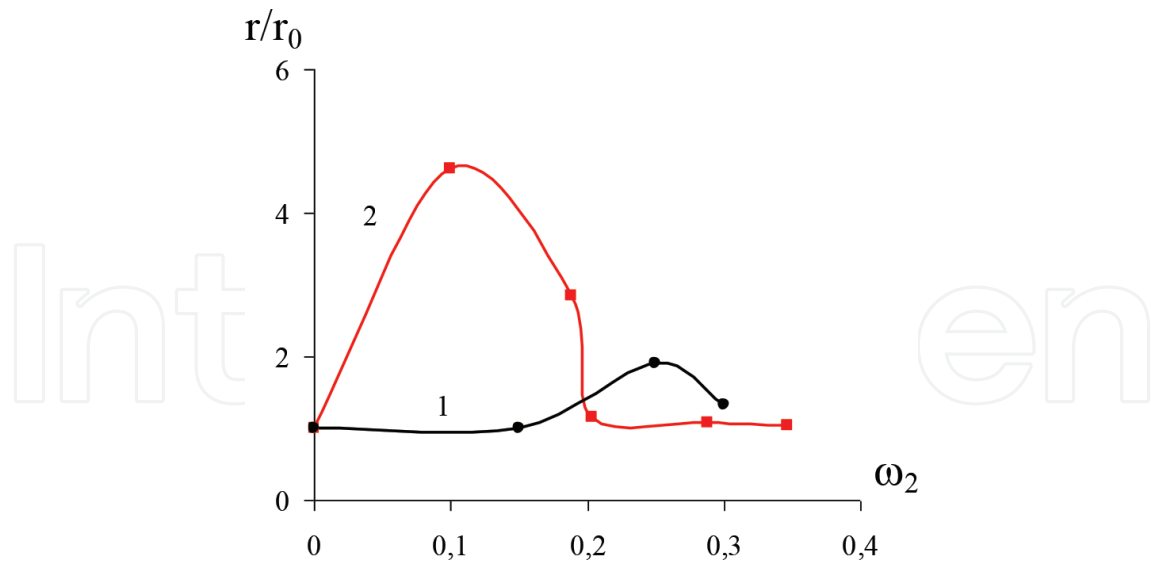
Ra is an arithmetic average of absolute values of deviations of a surface profile, Rq is an average quadratic absolute values of deviations of a surface profile, Rz is a height of roughnesses of a surface profile

**Table 1.** Parameters of the surface relief for the films HPC1 prepared from solutions in ethylene glycol in magnetic field and in its absence.

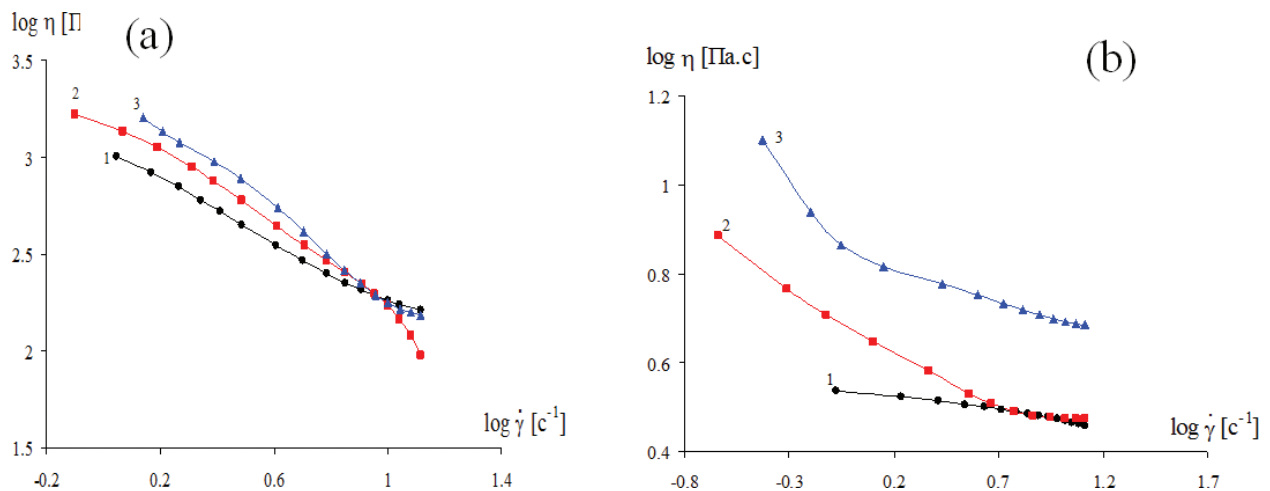


**Figure 10.** Concentration dependences of the diameters of supramolecular particles in the systems: HPC1-ethylene glycol, H = 0 (1) и 9.0 kOe (2) and EC-DMF, H = 0 (4) и 9.0 kOe (3). T = 298 K.

The solutions of HPC are non-Newtonian liquids, as manifested by a reduction in viscosity with an increase in shear rate. This result is in agreement with the data available for other liquid crystalline systems [70–76] and indicates that the initial structuring of polymer solutions is destroyed and that macromolecules and their associates orient along the direction of flow in the course of shearing. In addition, **Figure 11** shows that application of the magnetic field increases the viscosities of isotropic solutions. As it has been stated above it is connected with orientation of macromolecules in magnetic field. Such an orientation is related to the molecular diamagnetic anisotropy of macromolecules. As a result, supramolecular particles are formed, especially in the vicinity of the LC phase transition, and viscosity grows. But the magnetic field decreases the viscosities of anisotropic solutions (**Figure 12**). It is caused by easier orientation of macromolecules and supramolecular particles of anisotropic solutions in the magnetic field and also by the reduction of the particle sizes.

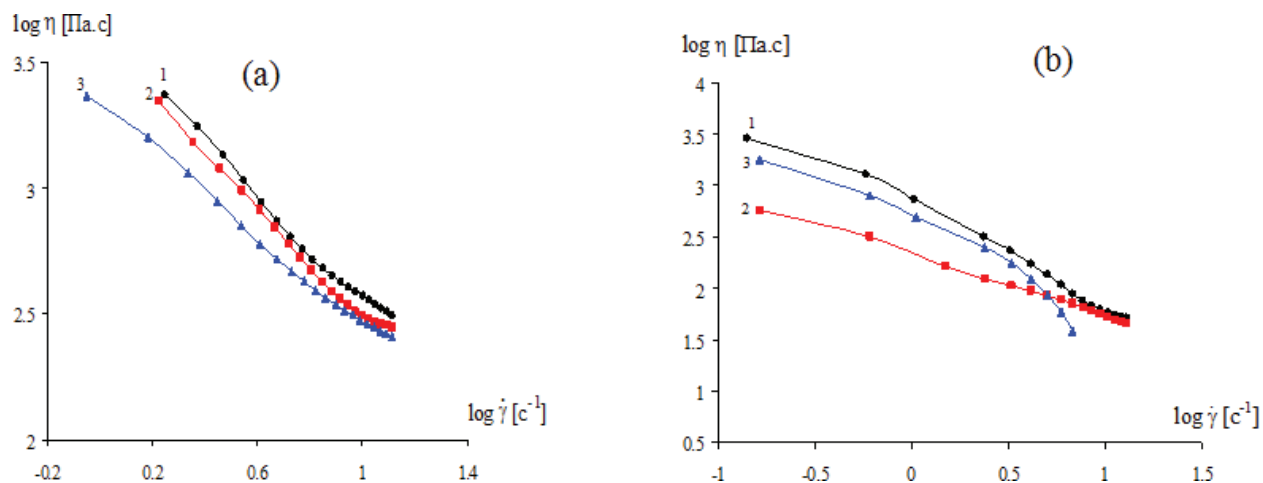


**Figure 11.** Concentration dependence of relative size  $r/r_0$  of supramolecular particles for systems: HPC1-ethylene glycol (1) and EC-DMF (2).



**Figure 12.** Dependences of viscosity on shear rate of isotropic solutions HPC1 in ethylene glycol:  $\omega_2 = 0.15$  (a), HPC2 in ethanol,  $\omega_2 = 0.15$  (b).

The above data were used to construct the concentration dependence of viscosity. In this case, the values of viscosity measured at a small shear rate  $2.5 \text{ s}^{-1}$  were chosen because, as was shown in [88–94], the concentration dependence of viscosity measured at precisely low shear rates is typical for anisotropic solutions. These dependences are described by curves with maxima for all studied systems. As the concentration of polymers is increased, the interchain interaction becomes stronger; as a consequence, supramolecular particles enlarge and viscosity increases. However, in the anisotropic region, viscosity decreases, in agreement with the literature data available for other systems having liquid crystalline transitions [88–94], and is related to the easier orientation of macromolecules and supramolecular particles along the direction of flow and to the reduction of the particle sizes. The magnetic field causes an increase in the viscosities of polymers solutions owing to the above-mentioned causes.

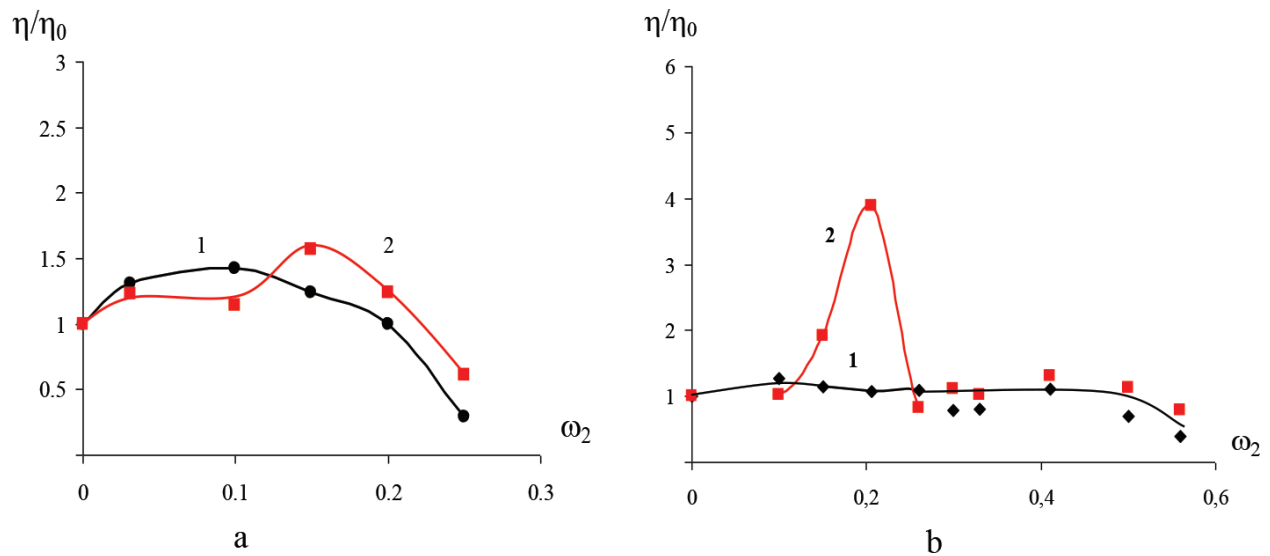


**Figure 13.** Dependences of viscosity on shear rate of anisotropic solutions HPC1 in ethylene glycol:  $\omega_2 = 0.30$  (a), HPC2 in ethanol,  $\omega_2 = 0.56$  (b).

Processes occurring during the flow of solutions in the magnetic field may be represented by the scheme (**Figure 6**). In quadrants I and III, the orientation of macromolecules coincides with the direction of flow and viscosity may decrease. In quadrants II and IV, the orientation of macromolecules is perpendicular to the direction of flow and viscosity should increase. Apparently, in this case, viscosity may either decrease or increase. When the force lines are directed parallel to the rotor-rotation axis (**Figure 6b**), macromolecules orient with their long axes along the axis of rotor rotation, that is, perpendicular to the direction of flow; as a result, viscosity may increase. Moreover, the macromolecules and supramolecular particles orient by their long axis along the rotor-rotation axis, i.e. layer-by-layer. In this case, an increase in viscosity can be compensated by reduction in the forces of viscous friction owing to the layer-by-layer arrangement of the macromolecules and particles.

The data were used to plot the concentration dependence of relative viscosity  $\eta/\eta_0$  (**Figure 14**), which reflects the effect of a magnetic field on the orientation of macromolecules and supramolecular particles in solutions ( $\eta$  and  $\eta_0$  are the viscosities in the presence of the magnetic field and in its absence, respectively).

As can be seen, the concentration dependences of  $\eta/\eta_0$  are described by curves with maxima. Analogous data for other systems involving liquid crystalline transitions (HPC-dimethyl sulfoxide, EC-DMF, hydroxyethyl cellulose-DMF, EC-DMAA, HEC-DMAA, HPC-DMF), were presented in some works [70–76]. The initial increase in  $\eta/\eta_0$  with concentration is related to an increasing number of magnetically sensitive macromolecules and supramolecular particles, a situation that results in intensification of the orientation processes in the field. However, with a further increase in the polymer concentration, the increasing density of the fluctuation network of entanglements begins to hinder the orientation processes and the influence of the field on the properties of solutions decreases. An analogous concentration dependence of relative size  $r/r_0$  of supramolecular particles (where  $r_0$  and  $r$  are the radii of light-scattering particles before and after magnetic field treatment of solutions, respectively) was found (**Figure 11**).



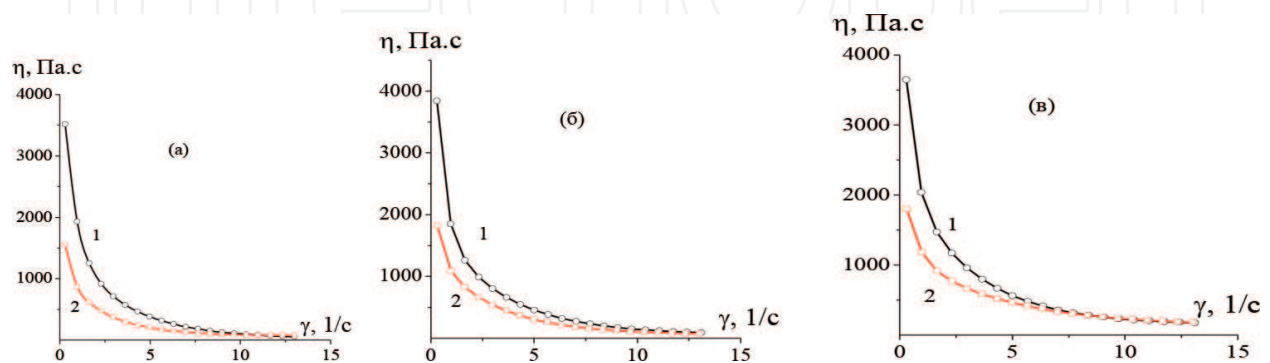
**Figure 14.** Concentration dependences of  $\eta/\eta_0$  for systems: (a) HPC1-ethylene glycol and (b) HPC2-ethanol.  $H_{||} = 3.6$  kOe (1) and  $H_{\perp} = 3.7$  kOe (2)  $\dot{\gamma} = 2.5 \text{ c}^{-1}$ .

## 2.4. The relaxation character of the rheological behavior of hydroxypropyl cellulose in ethylene glycol

The study of the viscosities of diluted and moderately concentrated solutions of HPC in ethanol and DMSO under the application of the magnetic field and in its absence showed that the loading and unloading curves coincide; that is, the hysteresis loop is absent. This result testifies that the structuring of the given solutions has time to recover after deformation.

**Figure 15** presents the rheological properties of the concentrated isotropic solutions of HPC in ethanol under loading and unloading. The same dependences are typical for more concentrated isotropic and anisotropic solutions of HPC in DMSO.

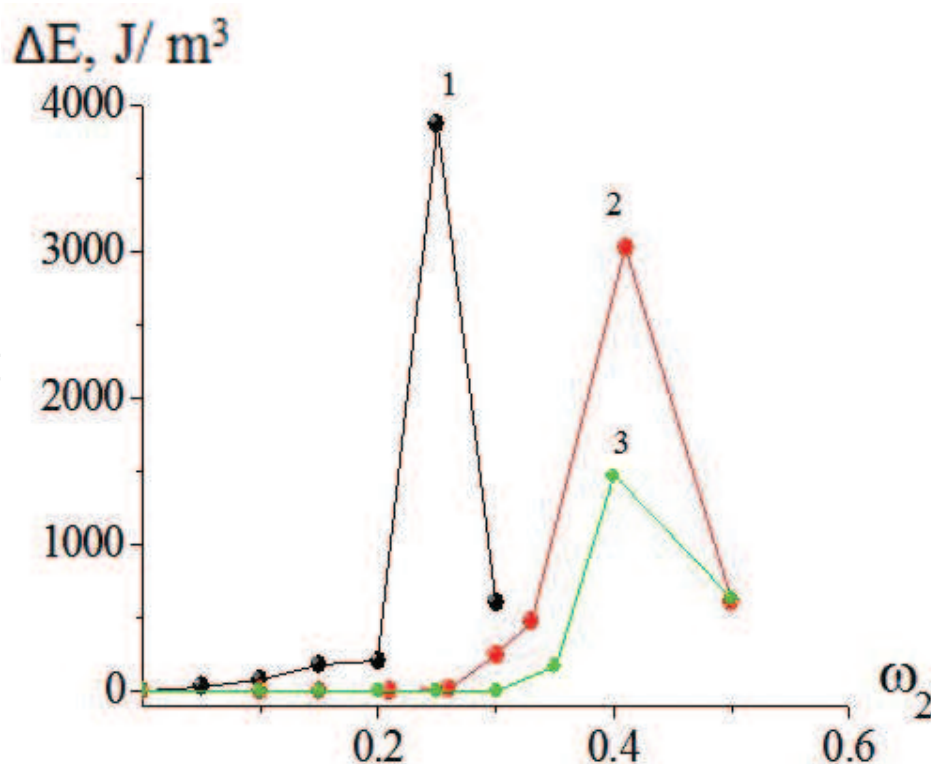
The loading and unloading curves do not coincide, and the hysteresis loop is present. This fact indicates that, in the concentrated solutions of HPC, the structuring of solutions has no time to recover after deformation. In fact, an increase in the concentration of a solution



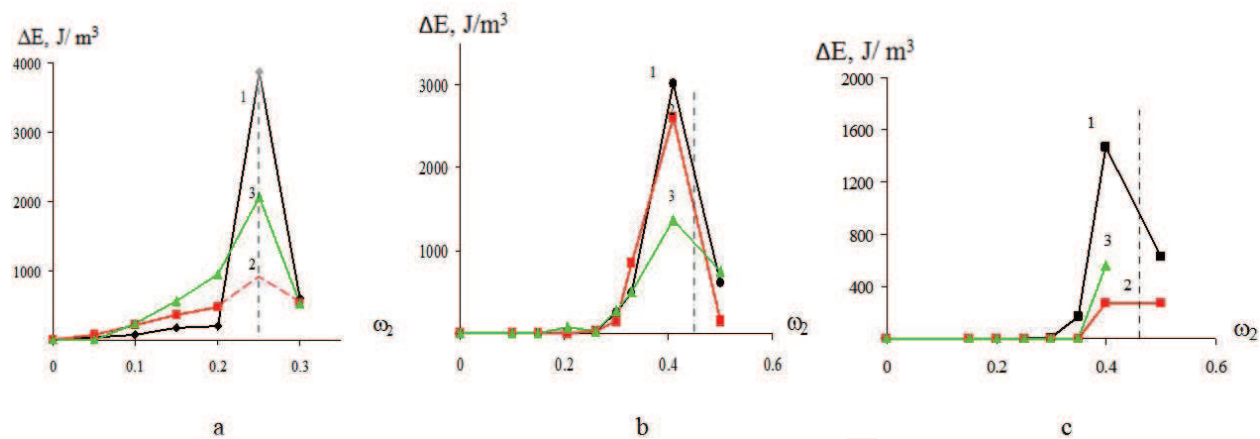
**Figure 15.** Dependence of viscosity on shear rate for the HPC2 solution in ethanol:  $\omega_2 = 0.41$  with (1) an increase and (2) a decrease in shear rate; (a)  $H = 0$ , (b)  $H_{||} = 3.6$  and (c)  $H_{\perp} = 3.7$  kOe.

entails an increase in viscosity, which is related to relaxation time  $\tau$  via the following relationship [95]:  $\eta = E\tau$ , where  $E$  is the shear modulus. For solutions with concentrations up to  $\omega_2 < 0.25$  (the HPC-ethanol system) and up to  $\omega_2 < 0.30$  (system HPC-DMSO), viscosities and relaxation times are smaller than those for more concentrated systems, the structuring of solutions has time to rearrange under the desired regime of change in the direction and value of shear rate, and the hysteresis loop is absent. However, for more concentrated solutions, the values of  $\eta$  and  $\tau$  are high enough; therefore, the structuring of systems has no time to recover and the loading and unloading curves do not coincide. In this case, the hysteresis loop is observed; its area characterizes the part of mechanical energy  $\Delta E$  irreversibly converting into heat energy, that is, mechanical losses in the unit volume of the sample per loading-unloading cycle.

**Figure 16** shows the concentration dependences of mechanical losses for studied systems. These dependences are described by curves with maxima. Maximum mechanical losses are seen in the vicinity of the isotropic - anisotropic transition of solutions. The same dependence is typical for the concentration dependence of viscosity of HPC solutions. In fact, as the concentration of HPC is increased, the interchain interaction becomes stronger; as a result, the sizes of supramolecular particles increase and viscosity grows. This situation hinders the orientation of macromolecules and supramolecular particles along the direction of flow, and, as a consequence, mechanical losses increase. However, in the anisotropic region, viscosity decreases because of the easier orientation of macromolecules and supramolecular particles along the direction of flow; as a result, mechanical losses decrease.



**Figure 16.** Concentration dependences of mechanical losses for the systems: (1) HPC1-ethylene glycol, (2) HPC2-ethanol and (3) HPC2-DMSO.



**Figure 17.** Concentration dependences of mechanical losses for the systems: (a) HPC1-ethylene glycol, (b) HPC2-ethanol and (c) HPC-DMSO.  $H = 0$  (1),  $H_1 = 3.6$  (2) и  $H_1 = 3.7$  (3). Dashed lines divide isotropic and anisotropic regions.

The similar dependences have been determined also for HPC solutions under magnetic field (Figure 17).

It is shown that the maximum of losses is observed in the concentration region near phase transition isotropic solution – anisotropic solution for the reasons described above.

### 3. Conclusion

The effect of a magnetic field on the viscosity of poly(ethylene glycol)-aerosol-iron nanoparticle and poly(dimethylsiloxane)-aerosol-iron nanoparticle magnetorheological suspensions is studied. The magnetic field leads to an increase in the viscosity of the suspensions by a factor of 20–300. The concentration dependence of the effect of magnetic field on the relative viscosity of the systems is described by a curve with a maximum.

The rheological properties, phase transitions, and structure of the hydroxypropyl cellulose-ethanol, hydroxypropyl cellulose-dimethyl sulfoxide, hydroxypropyl cellulose-ethylene glycol and ethyl cellulose-dimethylformamide systems have been studied in the presence and in the absence of a magnetic field. The regions of existence of isotropic and anisotropic phases and the concentration dependence of the sizes of supramolecular particles are determined. It is found that a magnetic field increases the viscosities of solutions. The concentration dependences of viscosity and particle size are described by curves with maxima. Loading and unloading curves do not coincide for solutions with the polymer concentrations  $\omega_2 > 0.25$  (the HPC-ethanol system),  $\omega_2 > 0.30$  (the HPC-DMSO system) and  $\omega_2 > 0.10$  (HPC1-ethylene glycol). The hysteresis loop is observed; its area characterizes the part of mechanical energy transformed into heat energy, i.e., mechanical losses. The concentration dependences of mechanical losses for studied systems are described by curves with maxima. The maximum mechanical losses are detected in the vicinity of the isotropic-anisotropic transition of solutions.



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